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Metaschoepite dissolution in sediment column systems – implications for uranium speciation and transport

William R. Bower^{1,2,3}, Katherine Morris², Francis R. Livens^{1,2}, J. Frederick W. Mosselmans⁴, Connaugh M. Fallon^{1,2,3}, Adam J. Fuller¹, Louise Natrajan¹, Christopher Boothman², Jonathan R. Lloyd², Satoshi Utsunomiya⁵, Daniel Grolimund⁶, Dario Ferreira Sanchez⁶, Tom Jilbert⁷, Julia Parker⁴, Thomas S. Neill², Gareth T. W. Law^{1,3*}

1. Centre for Radiochemistry Research, School of Chemistry, The University of Manchester, Manchester, UK, M13 9PL.

2. Research Centre for Radwaste Disposal and Williamson Research Centre, School of Earth and Environmental Sciences, The University of Manchester, Manchester, UK, M13 9PL.

3. Radiochemistry Unit, Department of Chemistry, The University of Helsinki, Helsinki, Finland, 00014.

4. Diamond Light Source, Harwell Science and Innovation Campus, Didcot, UK, OX11 0DE.

5. Kyushu University, Department of Chemistry, 744 Motooka, Nishi-ku, Fukuoka, Japan, 819-0395.

6. Swiss Light Source, Paul Scherrer Institute, Villigen, Switzerland, 5232.

7. Ecosystems and Environmental Research Programme, Faculty of Biological and Environmental Sciences, The University of Helsinki, Helsinki, Finland, 00014.

*Corresponding author: gareth.law@helsinki.fi

21 **ABSTRACT**

22 Metaschoepite is commonly found in U contaminated environments and metaschoepite-bearing wastes may
23 be managed via shallow or deep disposal. Understanding metaschoepite dissolution and tracking the fate of
24 any liberated U is thus important. Here, discrete horizons of metaschoepite ($\text{UO}_3 \cdot n\text{H}_2\text{O}$) particles were
25 emplaced in flowing sediment/groundwater columns representative of the UK Sellafield site. The column
26 systems either remained oxic or became anoxic due to electron donor additions, and the columns were
27 sacrificed after 6- and 12-months for analysis. Solution chemistry, extractions, and bulk and micro-/nano-
28 focus X-ray spectroscopies were used to track changes in U distribution and behavior. In the oxic columns, U
29 migration was extensive, with UO_2^{2+} identified in effluents after 6-months of reaction using fluorescence
30 spectroscopy. Unusually, in the electron-donor amended columns, during microbially-mediated sulfate
31 reduction, significant amounts of UO_2 -like colloids (>60% of the added U) were found in the effluents using
32 TEM. XAS analysis of the U remaining associated with the reduced sediments confirmed the presence of trace
33 U(VI), non-crystalline U(IV), and biogenic UO_2 , with UO_2 becoming more dominant with time. This study
34 highlights the potential for U(IV) colloid production from U(VI) solids under reducing conditions and the
35 complexity of U biogeochemistry in dynamic systems.

36 INTRODUCTION

37 Uranium (U) has been released into the environment through mining activities, weapons use, and *via*
38 authorized discharges and accidents at nuclear sites.¹⁻⁵ It is typically the largest radionuclide by mass in many
39 higher activity radioactive wastes that will be managed via geological disposal,⁶ where U exists in a range of
40 chemical forms.⁷ Uranium is radiotoxic, chemotoxic, long-lived (²³⁵U half-life = 703.8 x 10⁶ years, ²³⁸U 4.468 x
41 10⁹ years), and persists in the subsurface; thus, it poses a significant environmental and human health risk.^{8,9}
42 As such, understanding U behavior in the geosphere is essential.

43 Uranium is redox-active and its speciation typically controls its solubility and hence mobility. In oxic
44 environments, relatively soluble complexes of U(VI) are typically present.⁵ Under anoxic conditions, lower
45 solubility U(IV) species tend to dominate, with reaction end-products including UO₂ and poorly-crystalline
46 U(IV).¹⁰⁻¹² U(V) species have also been documented in environmental studies, but it typically
47 disproportionates.^{13,14} Uranium also readily sorbs to a range of minerals (e.g. Fe/Mn-oxy(hydr)oxides, -
48 sulfides, or phyllosilicates)¹⁵⁻²¹ and cell surfaces,^{22,23} or it can become incorporated into the lattices of neo-
49 forming mineral phases.^{24,25} Interestingly, incorporation of U(V) into neo-forming Fe oxy(hydr)oxides appears
50 to stabilise its redox state.^{24,26}

51 Overall, U(VI) reduction, sorption, or incorporation reactions in the geosphere can limit U migration in the
52 environment, but to date, U biogeochemistry studies have largely focused on mechanisms controlling U(VI)_(aq)
53 removal from solution (for example, see the review of Newsome et al., 2015).⁵ However, U(VI) solids have
54 also been released to the environment (often in particulate form), or they can concentrate naturally (e.g.
55 from U ores, placer deposits etc.). Our understanding of how these U solid phases behave in the environment,
56 and how they contribute to U transport is not well defined.

57 Metaschoepite (a U(VI) oxide) is a primary product of depleted uranium munition corrosion in former war
58 zones (e.g. Gulf and Balkan Wars) and at military test sites.²⁷⁻³⁰ It also forms upon oxidation of UO₂ in the
59 environment,^{31,32} and UO₂ can be formed at U contaminated sites *during* U(VI)_(aq) biostimulation,⁵ or be
60 dispersed in the environment during mining activities or through nuclear accidents.^{1,18,32,33} Large volumes of

61 uranium wastes, that include significant amounts of metaschoepite, may also be managed by either shallow
62 or deep disposal in the UK.^{7,34} Despite this, the environmental behavior of metaschoepite, and its impact on
63 U transport in complex, dynamic environmental systems is poorly constrained.

64 The objective of this study was therefore to track the stability of metaschoepite and the biogeochemistry of
65 any liberated U in complex sediment/groundwater systems, under realistic environmental conditions (i.e.
66 flowing groundwater, variable redox, dynamic sediment microbial communities). To do this, sediment
67 columns representative of the UK Sellafield Ltd. site were doped with discrete horizons of metaschoepite
68 particles. The metaschoepite was then subjected to groundwater flow for periods of up to 12-months; here,
69 the columns either remained oxic, or became progressively reducing due to the addition of electron donors.
70 Column effluent sampling during the experiments showed that metaschoepite was readily dissolved;
71 however, in the electron donor amended system, there was significant production of UO₂-like colloids during
72 microbially-mediated sulfate reduction. Sacrificial sampling of the sediments after 6- and 12-months of
73 reaction and bulk, micro- and nano-focus XAS and XRF analyses was used to track changes in solid U
74 speciation over time. Here, in oxic sediments U(VI) binding to Fe-bearing mineral phases was shown to be
75 important for longer term U(VI) retention. In the reducing sediments, a mix of non-crystalline U(IV) and
76 biogenic UO₂ governed U retention, but UO₂ appeared to be more prevalent over time. Trace U(VI) was also
77 detected in the reducing sediments, despite 10-months of sustained sulfate-reduction. The study highlights
78 the potential for U(IV) colloid production from U(VI) solids under anoxic conditions and the complexity of U
79 speciation in sediment systems.

80 MATERIALS AND METHODS

81 Metaschoepite Source

82 Synthetic metaschoepite powder was used as a metaschoepite source in sediment column studies. Prior to
83 use, the metaschoepite was sieved to 25-50 μm ; the “particles” in this size fraction were aggregates of
84 micron-scale platelets that formed electrostatically bound clusters. Uranium comprised 77 wt % of the solid,
85 yielding an average stoichiometry of $\text{UO}_3 \cdot 1.3\text{H}_2\text{O}$. Further detail on the metaschoepite is provided in the SI
86 (Section 1).

87 Sediment and Synthetic Groundwater

88 Sediment representative of the UK Sellafield Ltd. site subsurface was collected from a well-characterized field
89 site in Cumbria³⁵ (SI Section 2). The sediments were sampled from the unsaturated near surface (~5-10 cm
90 depth) and were confirmed to be oxic at the point of collection, and at the start of experiments (>97% of the
91 0.5 N HCl extractable Fe was present as Fe(III)). Prior to use in experiments, the sediment was sealed and
92 stored at 4°C for <2-months under a normal atmosphere. Autoclaved synthetic groundwater representative
93 of the Sellafield region,^{36,37} was used in the experiments (Table S1).

94 Column Design and Experimental Approach

95 A sediment / flowing groundwater column system was used so that the metaschoepite would be reacted
96 under conditions that are representative of those found in the environment, for example, where solid
97 contaminants would likely undergo gradual burial in soils / sediments, and experience water flow, ephemeral
98 redox conditions, and the influence of dynamic microbial communities. A schematic of the column set-up is
99 provided in the SI (Figure S4). The columns were made from acrylic tubing (18 x 4 cm; total volume ~214 cm^3)
100 and were packed with 240 g (12 cm vertical, ~151 cm^3) of sediment. 227 mg of metaschoepite (174 mg U)
101 was added into a 2 cm (vertical) horizon of the sediment (40 g sediment). The columns were terminated at
102 each end with layers of quartz sand (1 cm vertical) and glass wool (2 cm vertical), and then sealed with
103 DuranTM GL45 screwcaps with GL14 connectors. This set-up meant that the metaschoepite horizon was

104 placed 5 cm above the groundwater inlet, and 2 cm from the sediment base (see Figure S4). A peristaltic
105 pump (Watson-Marlow 205-U) was used to pump synthetic groundwater into the base of the columns, with
106 effluents then collected from the top of the columns. The groundwater pumping rate was $1.8 \pm 0.2 \text{ mL hr}^{-1}$
107 ($1.14 \times 10^{-6} \text{ m s}^{-1}$).³⁷

108 Two groundwater treatments were used: (i) oxic, and (ii) electron-donor amended. For the oxic treatment,
109 an air bubbler was used to maintain O_2 in the groundwater; for the electron-donor amended treatment, 1
110 mM (total) of acetate and lactate (50:50) was added and the groundwater was sparged with N_2 (30 min L^{-1}).
111 Prior work with these sediments has shown that similar electron-donor addition readily promotes
112 microbially-mediated bioreduction.^{35,37,38} Throughout the experiment, the pH of the influent groundwaters
113 was held between 7.2 and 7.4 via HCl addition. In the groundwater reservoirs, the concentrations of NO_3^- ,
114 SO_4^{2-} , and electron-donors (when present) remained within 5% of the starting concentrations between
115 weekly groundwater reservoir exchanges. Controls (systems with identical sediment/groundwater but
116 without any added metaschoepite) were also run.

117 **Sampling, Column Sacrifice, and Geochemical Characterization**

118 Duplicate sets of columns were reacted for 6- and 12-months. During this period, effluent samples were
119 collected at intervals by inserting a syringe into a port at the top of the column, with samples collected under
120 flowing Ar. The solutions were then centrifuged (5 minutes, $1.44 \times 10^4 \text{ g}$) and the resulting supernatant was
121 monitored for changes in pH, as well as the concentrations of NO_3^- , SO_4^{2-} , Fe, Mn, and U to track microbially-
122 mediated terminal electron accepting processes, changes in sediment geochemistry, and U dissolution/
123 migration from the metaschoepite source. Effluent pH was measured using calibrated electrodes (Mettler-
124 Toledo). Solution concentrations of NO_3^- , SO_4^{2-} , and Br^- (inert tracer) were measured by ion chromatography
125 (Dionex DX120) on filtered ($< 0.2 \mu\text{m}$ PES) samples. Iron, Mn, and U concentrations were measured by ICP-
126 MS (Agilent 7700x) from acidified (2% HNO_3) samples.

127 At experimental end-points (182- and 364-days), columns were uncapped under an Ar atmosphere and sub-
128 cores (18 x 1.5 cm) were taken along the length of each column using thin-walled Al tubes. The sub-cores

129 were immediately flash-frozen in liquid N₂ to preserve the sediment matrix, and then stored under Ar at -80°C
130 before further work. One sub-core was extruded and sectioned at 0.5 cm intervals; the resulting sections
131 were then digested in boiling *aqua regia* for elemental analysis by ICP-AES (Perkin-Elmer Optima 5300), or
132 leached in 0.5 N HCl for 60 minutes to estimate the proportion of bioavailable Fe(II) in the sediments.³⁹
133 Sections were also taken and kept frozen (-80°C) for bulk U *L_{III}*-edge XAS measurements. The other sub-core,
134 which had small perforations in the Al tubing to allow fluid exchange, was resin embedded with SpurrTM resin
135 under Ar, using a method designed to maintain the redox chemistry of the sediment and permit synchrotron
136 X-ray based μ -analysis.⁴⁰ The resulting resin-embedded core was then cross-sectioned, and 100 μ m thick
137 polished sections were prepared and mounted on quartz wafers for subsequent autoradiography and
138 synchrotron μ -focus analysis.

139 **Bulk and Spatially Resolved XAS/XRF Mapping**

140 Bulk U *L_{III}*-edge fluorescence XAS data were collected on select samples at 77 K on beamline B18 at Diamond
141 Light Source, UK (Si 111 double-crystal monochromator). Spectra were collected using either a 9 or 36
142 element Ge detector and calibrated using a Y-foil standard.

143 μ XRF maps and discrete-area XAS data were collected from resin embedded sediment thin-sections on
144 beamlines I18 at Diamond Light Source and X05-LA at the Swiss Light Source (see SI section 4 for further
145 details). μ XRF and XANES maps were collected from wafers (extracted perpendicular from the thin-sections
146 using a focused ion beam) on beamline I14 at Diamond Light Source (SI section 4).

147 **Autoradiography**

148 Autoradiographs, showing the distribution of radioactivity across the polished sections, were collected using
149 a TyphoonTM 9410 variable mode imager. Samples were exposed for 24-72 hours to a BAS-IP MS storage
150 phosphor screen (Amersham Biosciences) and scanned at 50 μ m resolution.

151 **Fluorescence Spectroscopy**

152 Uranyl emission spectra from selected aqueous samples were collected at 77 K following excitation at 420 nm
153 using a FP920 Phosphorescence Lifetime Spectrometer (Edinburgh Instruments) with a 450 W steady state
154 Xe lamp and a Hamamatsu R928P red-sensitive photomultiplier in air-cooled housing.⁴¹ All spectra were
155 corrected for the detector response and excitation source using the instrument correction files.

156 **Transmission Electron Microscopy**

157 TEM imaging with Selected Area Electron Diffraction (SAED) of nano-particulate phases present in effluent
158 samples were performed using a FEI Tecnai TF30 FEG analytical electron microscope with EDX spectrometer.
159 Effluent solutions from the columns were prepared for analysis on holey-carbon TEM grids (Agar Scientific)
160 using the method of Neill et al., (2018).⁴² Briefly, 2-3 drops (5 μ l) of centrifuged (5 minutes, 1.44×10^4 g)
161 effluent solution were pipetted onto the TEM grid and left to dry under an Ar atmosphere. This process was
162 repeated 2-3 times to accumulate sufficient colloids on the grid to permit analysis. The grid was then gently
163 rinsed with a few drops of isopropyl alcohol and finally fully dried (again under Ar) prior to TEM analysis. TEM
164 images/SAED patterns were processed and indexed using Fiji.⁴³

165 **DNA Extraction and Microbial Community Characterization**

166 DNA was extracted from select sediment samples from each column system to examine changes in the
167 microbial community structure during experimentation. Further details for microbial community analysis are
168 provided in SI section 5.

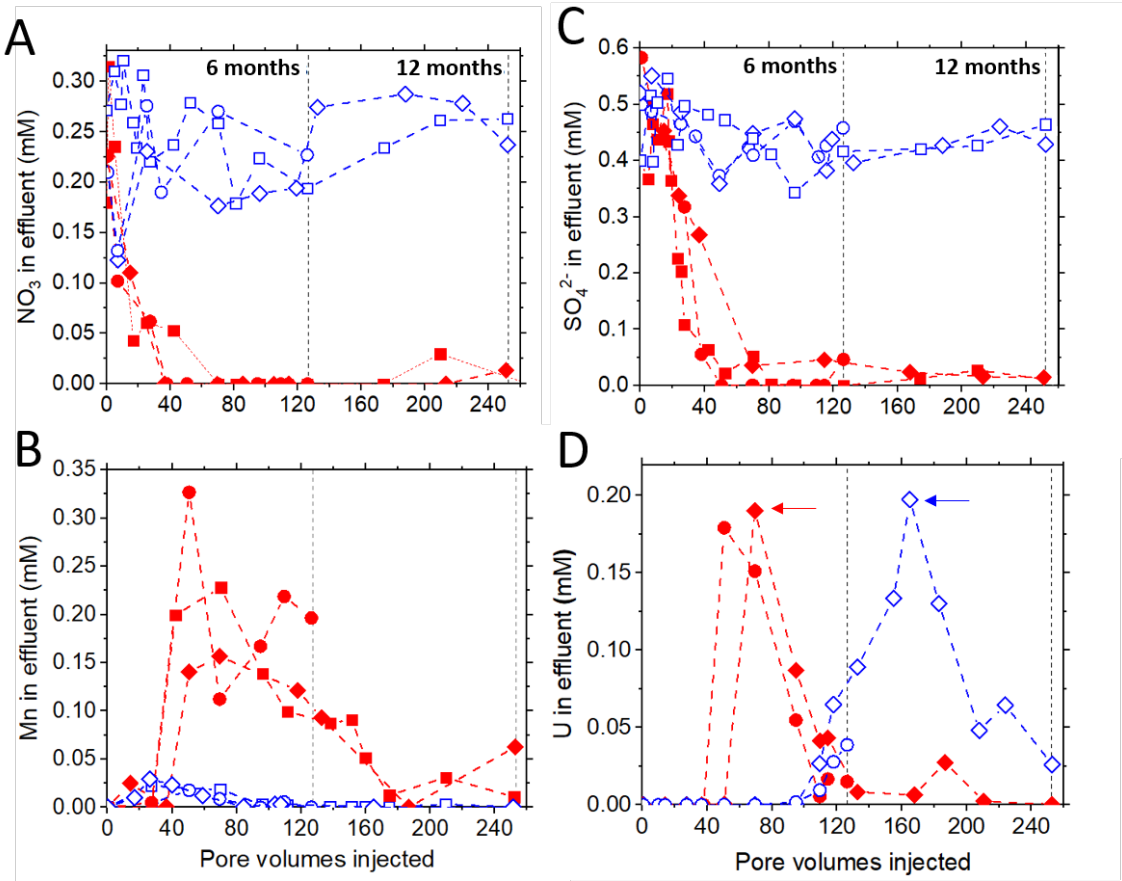
169 RESULTS AND DISCUSSION

170 Column Effluent Geochemistry and Microbial Ecology

171 A pore volume of ~62 mL for the column sediment was calculated from the Br⁻ tracer analysis (SI section 3).
172 This represented ~35% of the column's volume, giving a flow rate of ~0.7 pore volumes/day. Breakthrough
173 occurred after 112 hours (Figure S5). In all experiments, the effluent pH dropped marginally (lowest ~6.5 in
174 the oxic system) during the first month of reaction, presumably due to sediment buffering (SI Section 6). After
175 1-month, all of the effluents buffered to a pH between 7.5 and 7.9 for the remainder of the experiment, likely
176 due to bicarbonate alkalinity in the influent groundwaters (Table S1) and/or alkalinity generation in the
177 microbially-active sediment. It is unlikely that this small change in pH during the first month of groundwater
178 flow would have had a significant impact upon carbonate complexation of U, metaschoepite dissolution, or
179 mineral surface chemistry in this experiment. Stanley and Wilkin (2019)⁴⁴ have demonstrated comparable
180 metaschoepite solubility between pH 6-8.5 in the presence of 1mM sodium bicarbonate.

181 In the columns exposed to oxic groundwater with no added electron-donor (both control and U-containing
182 column systems), negligible changes in groundwater NO₃⁻, Mn, Fe, and SO₄²⁻ concentrations occurred (Figure
183 1). This suggests that these systems remained predominantly aerobic during the entire reaction period.
184 Uranium breakthrough from the oxic, metaschoepite amended columns was observed between
185 approximately 136-157-days (90-110 pore volumes; Figure 1D). In comparison, breakthrough of the
186 conservative Br⁻ tracer occurred after 112 hours (Figure S5), indicating that whilst the metaschoepite was
187 undergoing dissolution, U(VI) transport through the sediment was retarded. The first of two columns for this
188 system was sacrificed for solid phase analysis after 182-days, shortly after the initial U breakthrough (open
189 circles - Figure 1D). Effluent data indicated that after 182-days, ~3% of the initial metaschoepite source U
190 (~5.5 mg) had been eluted from the column via dissolution and groundwater transport (Figure 1). By the
191 experiment end-point (364-days), ~85% of the initial U (~148 mg) had been transported out of the column.
192 The microbial community in this U-doped column system, after 6- and 12-months of oxic groundwater flow,

193 remained remarkably similar to the microbial community of the fresh sediment, but a slight decrease in the
 194 proportion and diversity of Fe(III)- and sulfate-reducing bacteria was apparent (SI section 5.2).



195

196 **Figure 1.** Effluent porewater **(A)** NO₃⁻, **(B)** Mn, **(C)** SO₄²⁻, and **(D)** U for the oxic (no added electron-donor)
 197 groundwater system (blue, open symbols), and electron-donor amended groundwater system (red, closed
 198 symbols). Squares (open and closed) denote ‘control’ systems that did not contain any added U, diamonds
 199 and circles (open and closed) denote duplicate metaschoepite-doped column systems, where one of each of
 200 the duplicate columns was sacrificially sampled after 6-, and then 12-months. No effluent U was detected in
 201 the ‘control’ systems. Vertical dashed lines show timepoints at 6- and 12-months where columns were
 202 sacrificed, and solid phase geochemistry and micro-focus analysis was then completed. Arrows indicate the
 203 timepoint of effluent sampling for investigations of solution U speciation using TEM and luminescence
 204 spectroscopy. Iron was measured in the effluents and was at or close to the method detection limit without
 205 a discernible trend, so these data are not presented.

206

207 Continuous addition of 0.5 mM acetate and 0.5 mM lactate to the electron-donor amended column system
 208 resulted in a cascade of microbially-mediated terminal electron accepting processes. This was evidenced by
 209 clear trends in the effluent groundwater chemistry (Figure 1) and changes in the microbial community (SI

210 section 5.2). Dissimilatory NO_3^- reduction was apparent after 14-28-days (~10-20 pore volumes), with NO_3^- ,
211 which was continuously added at 0.3 mM, largely absent in the effluent groundwater after 58-100-days until
212 the end of the experiment (Figure 1A). Here, it is likely that a stable denitrifying community had developed
213 within the column, although given the sample resolution for microbial community analysis (SI section 5), it
214 was not possible to quantify this. As well as denitrification, evidence for metal-reducing conditions was also
215 observed, with soluble Mn appearing in the effluent after 36-58-days (~20-40 pore volumes) (Figure 1B).
216 Metal-reducing conditions were also reflected in an increased contribution from dissimilatory metal-reducing
217 bacteria in the microbial community at 182-days compared to the oxic control and starting material (SI
218 section 5.2). This was also accompanied by signs of microbially-mediated sulfate reduction, evidenced by a
219 reduction in the effluent sulfate concentration (continuously added at 0.5 mM) after 35-100-days (~40-70
220 pore volumes) (Figure 1C) and concurrent blackening of the sediment reflecting Fe-sulfide precipitation
221 (Figure 4). Indeed, near-total removal of sulfate was maintained from ~3-months until the end of the
222 experiment (Figure 1). Additionally, after 58-days, the sediment clearly blackened from the base of the
223 column upwards (Figure 4), indicating that a dynamic and robust sulfate-reducing zone had developed after
224 the exhaustion of bioavailable NO_3^- , Mn(III/IV), and Fe(III) in parts of the column. The microbial community
225 analysis data mirrored the column geochemistry, with a marked increase in *deltaproteobacteria* apparent in
226 the electron-donor amended columns after 182- and 364-days compared to microbial communities in the
227 fresh sediment and oxic column system (SI section 5.2; Figure S7). Data showed a relative increase in the
228 diversity and abundance of sulfate-reducing bacteria and methanogens in the electron-donor amended
229 columns, alongside a concurrent reduction in certain α -proteobacteria when compared to the fresh sediment
230 and the oxic column system (Figure S7).

231 Uranium was also present in the effluent from the electron-donor amended columns between 71-171-days
232 (~50-120 pore volumes) when clear evidence for strongly reducing, sulfidic conditions was apparent (Figure
233 1D). Surprisingly, U was eluted earlier than in the oxic column system. Indeed, the amount of U in the
234 electron-donor amended column effluent was significant, with ~60% (~106 mg) of the added U eluted by
235 182-days and ~70% (~124 mg) eluted by 364-days.

236 **Uranium Solution Chemistry/ Colloid Analysis**

237 The speciation of U in a sample of the groundwater from the oxic columns (taken after 234-days, U
238 concentration = 0.20 mM) was analyzed using luminescence spectroscopy (Figure 1D and S9). Here, the
239 spectrum was dominated by the characteristic vibrationally resolved emission profile of UO_2^{2+} between 450-
240 600 nm, confirming the solution speciation as dominantly UO_2^{2+} .⁴¹ In contrast, a sample with a similar U
241 concentration (0.19 mM) taken from the electron-donor amended system after 100-days had a 76%
242 reduction in the UO_2^{2+} emission intensity compared to the oxic experiment when the same instrument
243 settings were used (Figure S9). This indicates a reduced $\text{U(VI)}_{(\text{aq})}$ contribution to this spectrum compared to
244 the oxic sample.⁴¹ In addition, TEM and SAED analysis of the electron-donor amended effluent after 100-days
245 confirmed the presence of nano-crystalline U-bearing solids (Figure 2), with the SAED data having a structural
246 match to nano-crystalline, biogenic UO_2 , as observed by other studies.^{10,11,45-50} Taken together, the
247 luminescence and TEM data suggest that the electron-donor amended column effluent contained both
248 aqueous U(VI) and nano-crystalline UO_2 -like solids. However, the possible presence of U(VI) in/on the colloids
249 cannot be ruled out, and possible quenching of luminescence from colloid-bound U(VI) may also have
250 contributed to the reduced intensity observed from this sample (Figure S9). The presence of colloids was not
251 tested in the groundwater effluents of the oxic column systems.

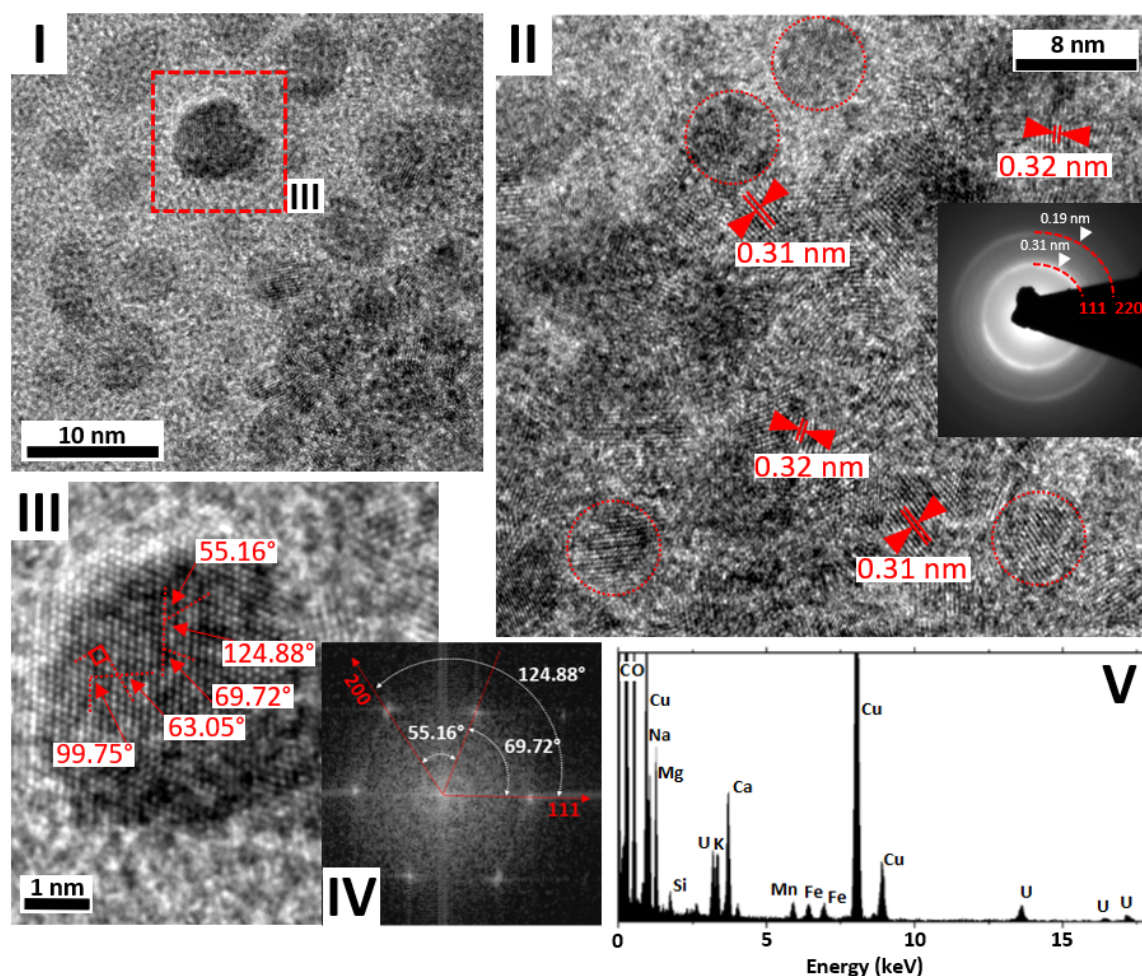
252 The observation of significant UO_2 -like colloid production from the metaschoepite source under sulfate
253 reducing conditions is unusual and suggests a significant pathway to U(IV) colloid formation compared to
254 biostimulation studies.⁵ Numerous authors have detailed the presence of U(IV) -bearing colloids in laboratory
255 studies.^{e.g. 46-52} Suzuki et al., (2002)⁴⁶ reported on the formation of biogenic UO_2 colloids from pure-cultures
256 of *Desulfosporosinus* spp. challenged with $\text{U(VI)}_{(\text{aq})}$ and electron donors, and from natural U contaminated
257 sediments. In the pure culture work, the UO_2 colloids (~1-3 nm in diameter) were attached to the bacterial
258 cell walls, indicating that they form at or near to the point of U(VI) bioreduction. Discrete UO_2 colloids and
259 aggregates were also found in this study. Similar work by Lee et al., (2010)⁴⁸ documented biogenic UO_2 colloid
260 formation, growth, and aggregation, and TEM analysis demonstrated that biogenic polymers caused the

261 aggregation. UO_2 colloids have also been documented to form on the surface of mackinawite (FeS) in the
262 presence of sulfate-reducing bacteria.⁴⁹ In that study,⁴⁹ the authors proposed a model where $\text{U(VI)}_{(\text{aq})}$ sorbed
263 onto the FeS surface. The U(VI) is reduced to U(IV) via a redox reaction with mineral bound Fe(II) ; then,
264 microbially-mediated regeneration of the Fe(II) allows for continued U(IV) accumulation on the FeS surface.
265 In turn, thus leads to UO_2 colloid nucleation and growth. Finally, UO_2 colloids have been reported to form
266 from corroding nuclear fuel ^{e.g. 51} and in experiments where $\text{U(VI)}_{(\text{aq})}$ is reacted with highly reactive Fe(II) -
267 bearing minerals.^{e.g. 52}

268 In this study, the use of a dynamic column system, combined with the complex biochemistry of the sediments
269 (i.e. competing biotic and abiotic process), means it is not possible to discern how the UO_2 -like colloids
270 formed from the metaschoepite in the electron donor amended system. However, the morphology and
271 grainsize of the U(VI) -solid may have played a significant role in forcing colloid formation. For example, rapid
272 metaschoepite dissolution would likely lead to high localised U concentrations for bacteria, or at reactive
273 mineral surfaces, encouraging colloid nucleation and growth.⁴⁸⁻⁵⁰ In turn, the groundwater flow in the
274 columns could have destabilised colloid growth / aggregation (e.g. concentration or physical effects), and/or
275 the propensity for colloid formation from the metaschoepite source may have outstripped the local supply
276 of aggregating agents, such as biogenic polymers.⁴⁸ Recent work in model abiotic systems has also shown
277 that Si can passivate UO_2 colloid surfaces, preventing their aggregation.⁴² Si was not added to the synthetic
278 groundwater used in the column experiments (Table S1), but Si would have been present at trace
279 concentrations in the groundwater due to silicate dissolution, and Si was present in the EDX analysis of the
280 UO_2 -like colloids (Figure 2). As such, Si may also have also played a role in passivating the surface of the UO_2 -
281 like colloids in this study.

282 Irrespective of the mechanisms, extensive UO_2 -like colloid formation from metaschoepite under sulfate-
283 reducing conditions is novel and additional work is now required to underpin a mechanistic understanding
284 of their formation and stability. Here, the impact of the U(VI) solid source (e.g. composition, grainsize,

285 morphology), biological interactions with this material, and colloid passivation mechanisms are clear areas
 286 for further research.



287

288 **Figure 2.** TEM analysis of the nanoparticulate U-bearing phase eluted from the electron-donor amended
 289 columns, sampled from effluent groundwater after 70 injected pore volumes (100-days of groundwater
 290 flow). (I-III) are a series of TEM images at sequentially increasing magnification. Dashed circles in (II)
 291 denote individual nanoparticles for context. A selected-area electron diffraction (SAED) pattern was collected from
 292 (II) (see inset) and the two primary reflections have been indexed according to the UO_2 structure. An
 293 approximate lattice constant of 0.546 nm was calculated based on SAED analysis, close to that of UO_2 (~0.547
 294 nm at ambient temperature).⁵³ Panel (III) shows a high-resolution image of a single colloid, with interplanar
 295 angles indicative of the UO_2 structure superimposed. (IV) FFT of the area displayed in (III). (V) EDX analysis
 296 across an aggregation of colloids showed U as one of the most abundant elements, after C and Cu (as inherent
 297 components of the TEM grid); further, K, Ca, and Mg were present likely as precipitated salts from the
 298 synthetic groundwater. Trace amounts of Mn, Si, and Fe were also measured as expected from complex
 299 environmental samples.

300

301 **Acid Extractions and Solid Phase Geochemistry**

302 Sediment samples from two timepoints (182- and 364-days) from each of the oxic and electron-donor
303 amended systems were assessed for bioavailable Fe(II) using 0.5 N HCl extractions (SI Figure S10A).⁵⁴ Here
304 both oxic columns showed only trace Fe(II) present in the sediments. This, coupled to the effluent and
305 microbial community data (Figure 1 and SI section 5.2) confirmed that both of the columns remained oxic
306 throughout the experiment. In contrast, after 182-days of electron-donor amendment, this column system
307 showed 75-95% 0.5 N HCl extractable Fe(II) throughout the length of the column (Figure S10A), confirming
308 significant reduction of Fe(III) to Fe(II) and retention of the Fe(II) within the sediments (>90% Fe(II) after 364-
309 days). Additionally, aqua regia extractions confirmed that in both electron-donor amended columns the
310 sediment-associated Mn concentrations were generally lower than comparable oxic columns (Figure S10C),
311 consistent with the observed reductive mobilization of Mn (Figure 1).

312 Sediment associated U profiles were also measured from *aqua regia* lixiviants and highlighted differences in
313 gross U retention and migration / U loss under the different groundwater treatments. After 182-days flow
314 under oxic conditions, ~70% of the U originally added in the metaschoepite source was recoverable from the
315 column sediments. The U had migrated from the source throughout the entire length of the column (U
316 concentrations varied between 500-1000 mg kg⁻¹ up to 6 cm beyond the initial metaschoepite source) (Figure
317 S10D). However, the U mass balance between the sediment extractions and effluents for this system after
318 182-days was poor (~27% of the added U was unaccounted for). This may reflect heterogeneity in U
319 distribution in the sediments after metaschoepite dissolution (see Figure 3) relative to the coarse-nature of
320 sediment sampling for the aqua-regia extractions. After 364-days under oxic conditions, the solid-phase U
321 concentration had then fallen to between ~150-250 mg kg⁻¹ throughout the column (Figure S10D),
322 presumably as a result of the continued dissolution and/or mobilization of particle associated/sediment-
323 bound U(VI). This meant that ~21% of the originally added U remained extractable from the sediment after
324 1-year of oxic groundwater flow. The U mass balance between the sediment and effluents for this time-point

325 was better (~106% of the added U accounted for); as such, the majority of the metaschoepite derived U had
326 been transported out of the columns.

327 In the electron-donor amended columns after 182-days of reaction, the transport of UO₂-like colloids out of
328 the columns (Figure 1D and Figure 2) meant that the total sediment extractable U was significantly lower
329 than its oxic counterpart (only 30% of the U added in the metaschoepite remained in the sediments). This
330 decreased to 21% after 364-days. The U mass balance (sediment extractions and effluents) for the two
331 electron donor amended columns was 90 and 91%, respectively.

332 **Bulk X-ray Absorption Spectroscopy**

333 Select samples were analyzed using bulk U *L_{III}*-edge XANES and EXAFS. In the oxic systems, at 182-days, the
334 sediments downflow from the initial metaschoepite horizon were sampled. For the bio-reduced systems,
335 sediments from both within and downflow of the horizon were sampled at 182- and 364-days (see Figures 3
336 and 4, SI Figures S11 and S12, Spectra A-E). In order to gain insights into the U oxidation state changes in
337 these complex samples, XANES data were analyzed by Iterative Target Factor Analysis (ITFA) (Figure S11).⁵⁵
338 Sediments from the oxic system showed U(VI) speciation as expected, and sediments from the electron-
339 donor amended systems showed evidence for partial reduction, with ITFA suggesting between 30-80% U(IV)
340 across the samples. Here, the amount of sediment associated U(IV) varied with distance from the
341 metaschoepite source, and the overall proportion of U(IV) increased from 182- to 364-days (Figure S11). For
342 the oxic system, bulk EXAFS fitting parameters and best-fit results confirmed uranyl-like adsorption to the
343 sediment in a sample taken from within the metaschoepite source horizon. Scattering contributions from C
344 and Fe shells indicated uranyl complexation at the surface of Fe-oxy(hydr)oxides in the presence of
345 carbonate. U-C/Fe distances correlate to expected distances for edge sharing carbonato-complexes at the
346 surface of iron oxy(hydr)oxides.⁵⁶ Uranyl retention by sediments in this manner is well documented, as U(VI)
347 has been widely shown to sorb (bidentate edge/corner sharing) to a range of Fe/Mn-oxy(hydr)oxides.^{21, 56-60}
348 The dominant Fe-oxides in the sediment used in this study are hematite and goethite, which appear to be
349 effective at sorbing U(VI) released from metaschoepite.⁵⁶⁻⁵⁸

350 For the electron-donor amended systems, a contribution to the spectra from an axial O shell at ~ 1.8 Å (uranyl
351 coordination) was varied based on ITFA fitting of the XANES (Table S3) and this approach provided good fits.
352 In the electron-donor amended column system after 182-days of groundwater flow, a uranyl contribution to
353 the bulk EXAFS could still be modelled for samples taken from within the initial metaschoepite source
354 horizon, as well as 3-3.5 cm downflow from the source, but its importance was reduced relative to U(IV)-O
355 coordination (Figure S12, Table S4; spectra B and C). Both spectra could also be modelled with an improved
356 fit that included contributions from Fe and C shells. An oscillation was also visible in the Fourier transform at
357 ~ 3.8 Å for the 182-day metaschoepite source horizon sample (spectrum B, Figure S12); this may be indicative
358 of a U-U shell from nano-crystalline UO_2 ,^{10,11,46,47} however, the addition of a U-U shell did not yield a significant
359 statistical improvement to the overall model fit for this spectrum.

360 After 364-days of reaction in the electron-donor amended column system (Figure S12, Table S4; spectra D
361 and E), the inclusion of partial uranyl O coordination was still statistically significant, suggesting that even
362 after 10-months under sulfate-reducing conditions, some U(VI) was still present in the sediments. The sample
363 within the original metaschoepite source horizon was modelled with a significant U-U backscatter shell, with
364 3.2 U atoms at 3.84 ± 0.03 Å, suggesting that nano-crystalline UO_2 formation increased with time.^{e.g.61}
365 Interestingly, the sample at a greater distance from the original metaschoepite source horizon did not show
366 an improved fit with inclusion of a U-U backscatter shell at ~ 3.8 Å, suggesting no strong evidence for nano-
367 crystalline UO_2 at distance from the original metaschoepite source horizon.^{11,12} The formation of biogenic,
368 non-crystalline U(IV)^{10,11} as a U(VI) reductive end-point, separate from that of UO_2 formation, is influenced
369 by the species present in the experiment. The concentration of organic ligands, phosphate and the availability
370 of surfaces of certain Fe(II)-minerals promote formation of non-crystalline U(IV) over UO_2 formation.^{10,12,61-64}
371 An Fe backscattering shell could also be modelled for all bulk EXAFS spectra collected from the electron-
372 donor amended columns except for spectrum D (Table S4).

373 Overall, bulk EXAFS fitting for samples from the electron-donor amended column system shows a decrease
374 in U(VI) like coordination with time. After 1-year, at the base of the column where sulfate-reducing conditions

375 have existed for the longest, UO_2 ingrowth dominates; with monomeric or non-crystalline U(IV) present
376 further from the initial U and groundwater (and hence sulfate) source.

377 **High Resolution Autoradiography and μ -focus XRF and XAS**

378 Data from the oxic column thin-section, sampled after 182-days of groundwater flow, are shown in Figure 3.
379 At the 50 μm pixel resolution provided by the autoradiographs, U migration from the metaschoepite source
380 along the groundwater flow-path is clear. After 182-days in the oxic column, a concentrated zone of
381 radioactivity extends for ~ 4 cm beyond the metaschoepite source region (Figure 3-II). Beyond this, the activity
382 becomes diffuse. μXRF mapping of selected areas within this zone showed a non-uniform distribution of U
383 throughout the sample. Many areas showed U enrichment in regions also rich in Fe and Mn (e.g. Figure 3;
384 map 1) as well as in the sediment matrix between larger mineral grains (i.e. clay/organic rich areas) (e.g.
385 Figure 3; Panel 4). Clays and organic matter commonly sorb U(VI).^{57,65} The area of highest U retention in the
386 thin-section was found along a horizontal, linear feature in the autoradiograph. XRF mapping of this feature
387 (Figure 3; maps 2 and 3) indicates it is a root fragment, due to the presence of life-supporting nutrients such
388 as Cu and Zn^{66,67} and consistent with organic material acting as sorption sites for U(VI) in sediments.^{68,69}
389 Elemental correlation plots from broad-scale maps (Figure 3-IV) reveal that, of the elements resolvable by
390 μXRF mapping, Fe and Mn show the strongest positive correlations with U in these oxic systems. This is also
391 reflected in bulk EXAFS modelling where fits show Fe backscatters are possible, suggesting sorption to Fe-
392 oxides⁵⁹ (Table S4). Zinc and Cu also give an indication of possible U uptake onto organic matter, and a
393 correlation between U and Sr may be indicative of uranyl association with carbonate or clay minerals.⁶⁹
394 μ -focus XANES measurements from the same thin-section (Figure S11, spectra F-I) showed that U(VI) was
395 dominant ($>90\%$) throughout the column. Corresponding μEXAFS measurements could be modelled with
396 uranyl O coordination, similar to that described for the bulk-EXAFS measurement from this column system
397 (see SI section 9 for the full dataset and fitting parameters). Further, μ -focus spectra F-I (Figures 3 and S13;
398 Table S5) could be modelled as uranyl complexes binding to the surfaces of Fe-bearing minerals consistent
399 with U(VI) sorption to Fe-oxides.⁵⁵⁻⁵⁹ The fit for spectrum I, collected from the root fragment, was significantly

400 improved by the incorporation of a U-C scattering path at $2.91 \pm 0.02 \text{ \AA}$; this may also reflect carbonato-
401 complexed U(VI).^{21,56,70} Evidence for a U-C path is also apparent in the Fourier transforms of spectra F and H,
402 but the incorporation of this path was not statistically valid (Table S5).

403 In the electron-donor amended column systems, and consistent with bulk geochemical measurements
404 (Figures 1 and S10), the autoradiographs (Figure 4) displayed a 'patchy' distribution of radioactivity in both
405 the 182- and 364-day columns, highlighting discrete regions of U retention following the onset of sulfate-
406 reducing conditions. XRF maps revealed that after 182-days of groundwater flow, U was found in discrete
407 zones in the sediment matrix (Figure 4, maps 1-4) in a similar manner to that described for the oxic system
408 (U correlated with Fe- and Mn-rich phases, as well as biomarker elements like Zn and Cu). Further, more
409 diffuse areas of U enrichment were found with distance from the metaschoepite source region, as well as
410 additional areas of discrete U enrichment (Figure 4; maps 1-3).

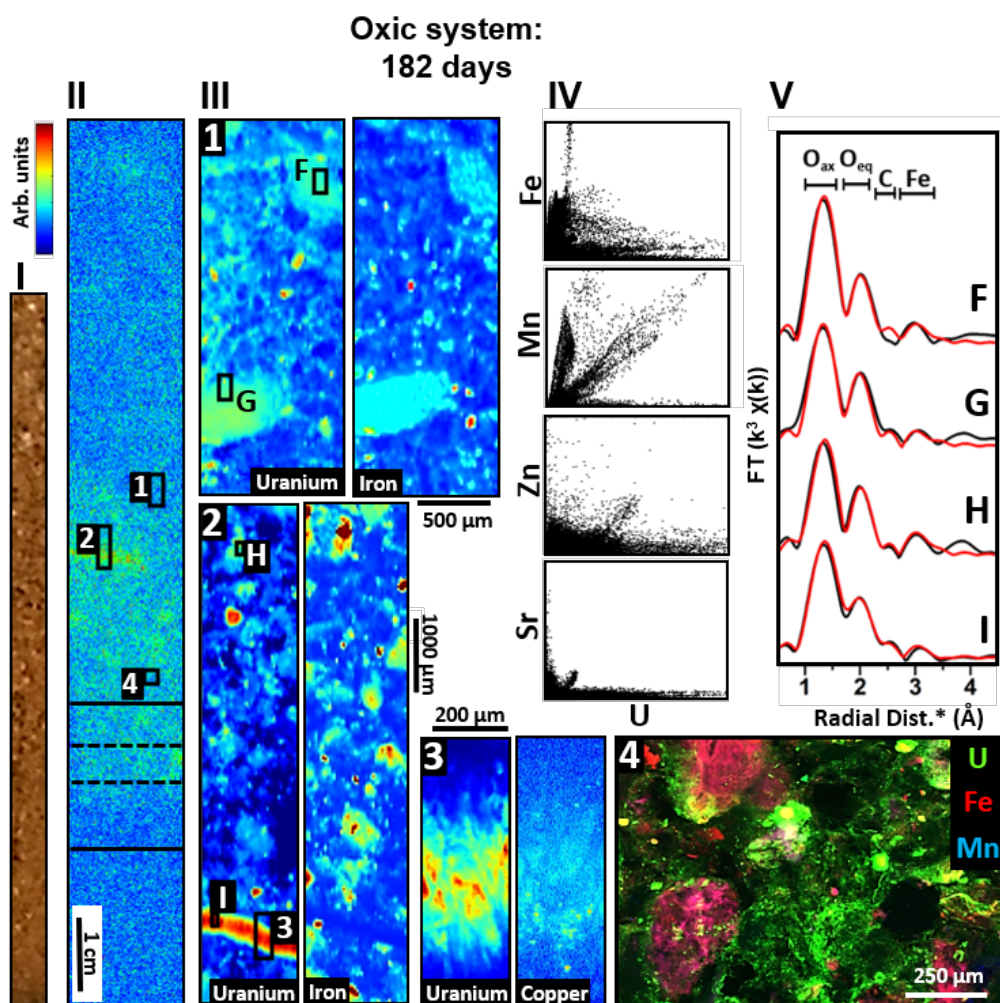
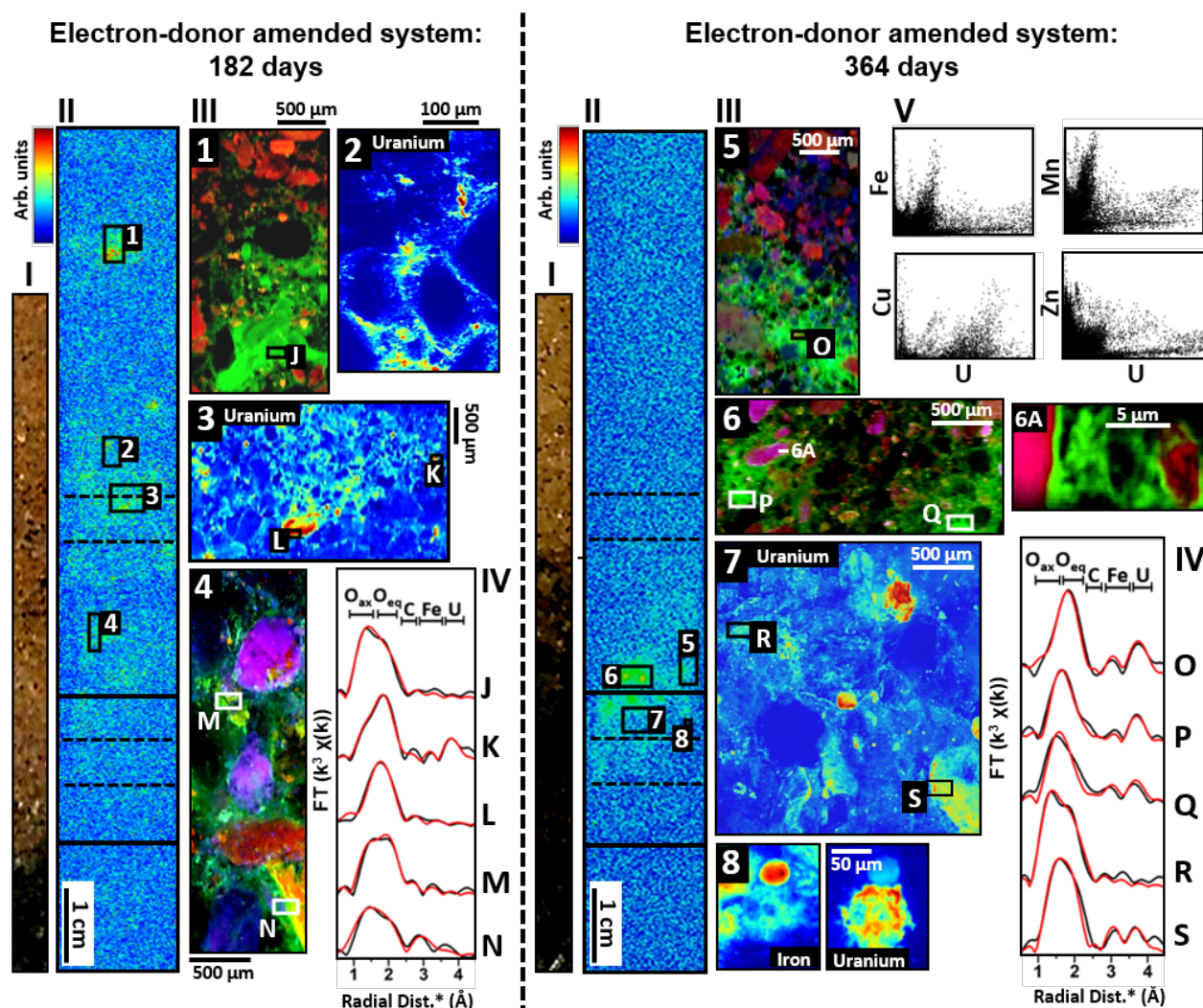


Figure 3. (I) Color photograph (10 cm vertical) of the oxic column after 182-days. Note the uniformity of orange / brown color along the core's length, indicative of Fe(III) dominating throughout. (II) Autoradiograph of the resin-embedded, cross sectioned column profile showing radioactivity distribution along the sediment core ('warmer' colors denote higher radioactivity). Solid horizontal lines on the autoradiograph mark the zone of initial metaschoepite particle emplacement. Most of the U had migrated from this zone after 182-days. Dashed horizontal lines denote the horizon sampled for bulk U L_{III}-edge XANES and EXAFS (Spectrum A in relevant Figures and Tables). Numbered boxes within the autoradiographs correspond to μ-focus XRF maps in (III). Maps in (III) are either displayed as element-specific color panels (where warmer colors denote relative higher concentrations) or as multi-element RGB maps (where green = U, red = Fe, blue = Mn, and color intensity denotes relative proportions of each element). (IV) Scatter plots denote correlations between major elements (Fe, Mn, Zn, Sr) and U from broad-scale maps over areas that encompass those shown. Positive correlations denote co-location of the elements at differing concentrations. (V) μ-focus (F-I) U L_{III}-edge EXAFS (k³ weighted Fourier transforms displayed for clarity, full datasets are presented in SI Section 9) from discrete points marked by lettered boxes on the XRF maps. *denotes that the Fourier transform is non-phase corrected. Bracketed regions above the plots show the expected peak positions for O, C and Fe and U scatterers (non-phase corrected).



429

430 **Figure 4.** For each timepoint (182- and 364-days) from the electron-donor amended column system: (I) Color
 431 photographs showing the sediment profiles (10 cm vertical). Note the ingrowth of FeS (blackening) along the
 432 flow direction (base to top). (II) Full-length autoradiographs of the resin-embedded, cross sectioned
 433 sediments showing radioactivity distribution in the columns (acquisition times varied for clarity, see SI Figure
 434 S11 for U concentrations in digests). Solid horizontal lines denote the region of initial metaschoepite source
 435 emplacement, dashed horizontal lines denote the horizons from which bulk U L_{III} -edge XANES and EXAFS data
 436 were collected (Spectra B-E in relevant Figures and Tables). Numbered boxes within the autoradiographs
 437 correspond to μ -focus XRF maps in (III). Maps in (III) are either displayed as element-specific color panels
 438 (where warmer colors denote relative higher concentrations) or as multi-element RGB maps (where green =
 439 U, red = Fe, blue = Mn, and color intensity denotes relative proportions of each element). XRF map 6A is a
 440 nano-focus map (pixel size 100 nm) of a FIB section extracted perpendicular to white line in XRF map 6 (see
 441 Figure S15 for details). Boxes marked J - S, within the XRF maps denote regions from which μ -focus U L_{III} -edge
 442 XAS data were collected, with EXAFS shown in (IV) (k^3 weighted Fourier transforms displayed for clarity, full
 443 datasets and XANES are presented in SI Section 9). *denotes that the Fourier transform is non-phase
 444 corrected. Bracketed regions above the plots show the expected peak positions for O, C and Fe and U
 445 scatterers (non-phase corrected). (V) Scatter plots denote correlations between major elements (Fe, Mn, Zn,
 446 Cu) and U from broad-scale maps over areas that encompass those shown. Positive correlations denote co-
 447 location of the elements at differing concentrations.

448 After 364-days, most of the U retained on the sediments was largely present in a discrete horizon ~1 cm
449 above the initial metaschoepite source. Here, some U was co-located with Fe-rich mineral grains (Figure 4;
450 maps 6 and 7), indicating that U may interact with reactive Fe at mineral surfaces. A proportion of the U was
451 also matrix-bound (i.e. not associated with mineral surfaces), possibly being retained by clays and/or organic
452 matter along groundwater flow paths (Figure 4, map 7).

453 μ XANES measurements from the 182-day, electron-donor amended system (Figure S11, spectra J-N) showed
454 that U(IV) accounted for 40-60% of the U on the solid phase. μ EXAFS also revealed a range of mixed
455 U(IV)/U(VI) species (Figure 4 and S13, Table S6). Structures indicative of non-crystalline U(IV) could be
456 modelled for several spectra. Only spectrum K, collected from a U hotspot ~7.5 cm from the sediment base,
457 could be confidently modelled using a U-U backscatter. Most spectra collected from the 182-day thin-section
458 could be modelled with C and/or Fe backscattering shells (Table S6). Combined, the bulk and μ EXAFS data
459 suggest that monomeric U dominates in this sediment system during the early stages of bioreduction. Again,
460 Fe surfaces have also been implicated as important sites for both U(IV) and U(VI) retention.⁷¹

461 After 364-days in the electron-donor amended system, the residual U in the column was primarily contained
462 within the black-colored zones where sulfate reduction had occurred (Figure 4). The proportion of U(IV) in
463 this region, as modelled from the μ XANES data (Figure S11, spectra O-S), was higher (63-80%) likely due to
464 longer periods under reducing conditions. Corresponding μ EXAFS data (Figures 3 and S13; Table S7) were
465 best modelled with small contributions from uranyl-like O backscatters emphasizing that only residual U(VI)
466 remained in this system. Backscattering shells of C and/or Fe and increased contributions from UO₂ like U-U
467 backscatters could also be modelled. For example, spectra O, P, Q, and S (Figure 4) could all be modelled with
468 a U-U path concurrent with nano-crystalline, biogenic UO₂. Evidence for non-crystalline U(IV) in these
469 horizons was scarce; only spectrum R (65% U(IV)) showed no evidence of a U-U scattering contribution. When
470 considered alongside the bulk EXAFS data for this column system, it appears there is a preferential growth of
471 nano-crystalline UO₂ near the base of this system with sustained bioreduction.

472 Mechanisms for the preferential formation of 'monomeric' U(IV) vs. biogenic UO₂ are complex. Studies have
473 shown the end-product of microbial U(VI) reduction to be dependent both upon the local microbiology and
474 geochemistry. Indeed, systems containing higher ionic strength media (elevated concentrations of chlorides
475 and phosphates) have yielded an increased contribution from non-crystalline U(IV) from the same
476 bioreducing cell cultures.^{10,11,62} Studies have also suggested that UO₂ formation is prohibited due to the
477 retention of U by cell biomass during reduction.^{11,64} In phosphate-free systems, Gram-positive bacteria
478 preferentially produced non-crystalline U(IV) in direct contrast to Gram-negative bacteria, which produced
479 nano-particulate UO₂ under the same conditions, the differences proposed to be a result of cell envelope
480 architecture.⁶² The formation of discrete U(IV) phosphate and carbonate phases must also be considered in
481 dynamic systems like those presented here, although no evidence is apparent in the μ EXAFS, and no P was
482 supplied in the groundwater. Significant variations in binding site, local biomass, local porewater chemistry,
483 and microbiology are therefore competing factors within discrete micro-environments to favor the formation
484 of a specific end-member. Here, the interplay of all these factors on the micro-to-nano scale must be
485 considered, however it is difficult to isolate a specific mechanism of non-crystalline U(IV) formation in these
486 dynamic systems. In this case, as observed previously,^{72,61} residence time (i.e. ageing of the non-crystalline
487 U(IV) fraction) likely accounts for the increase in nano-crystalline UO₂.

488 **Nano-focus XRF and XANES mapping**

489 Variations in U speciation were also present at the nanometer scale (Figure S14). The extraction of a wafer
490 of U contaminated sediment from the electron-donor amended column sediment (364-day) thin-section,
491 along a Fe-oxide grain boundary (Figure 4, map 6A), permitted nano-XRF and XANES mapping at the newly
492 commissioned Diamond Light Source Hard X-ray Nanoprobe (Figure S14). Discrete U L_{III}-edge XANES data
493 from this sample have been grouped by subtle differences in the spectra, and the result is a nanometer-scale
494 U speciation map. Figure S14 indicates the presence of up to three discrete groups of spectra identified within
495 the 10 μ m x 5 μ m FIB section; the most oxidized (blue and green) are more closely associated with the regions
496 of highest U concentration, along the boundaries of Fe-oxide grains.

497 **Implications**

498 This work has shown that an array of competing mechanisms control U migration and fate in complex
499 sediment systems during metaschoepite dissolution. Under oxic conditions, metaschoepite dissolution
500 resulted in significant $U(VI)_{(aq)}$ transport; however, $U(VI)$ reaction with Fe-bearing sediment species retarded
501 groundwater U transport and resulted in long-term (~1-year) $U(VI)$ retention. During metaschoepite
502 dissolution under anoxic conditions, significant amounts of UO_2 -like colloids were produced. As colloids are
503 known to enhance contaminant transport through the geosphere, this finding may be significant (e.g. for the
504 management of sites contaminated with depleted U penetrators, mining sites, or for the geodisposal of
505 metaschoepite containing wastes). However, further work is required to document the colloid formation
506 mechanism(s) and stability, and this should include defining the role that the solid U source (i.e. chemical
507 composition, surface morphology etc.) plays in controlling / instigating U colloid production, and the relative
508 importance of biotic^{46,48} vs. abiotic^{49,52} UO_2 colloid formation mechanisms. Under anoxic conditions, micro-
509 to-nano-focus XAS also revealed that $U(VI)$, non-crystalline $U(IV)$, and UO_2 were all retained in the sediment
510 after metaschoepite dissolution, and UO_2 appeared to be a more important $U(IV)$ product with added time.
511 This may be significant in terms of uranium's general biogeochemistry, as it is thought that UO_2 may be more
512 resistant to oxidative remobilisation, but clearly in this study, this is tensioned against significant $U(IV)$ colloid
513 production. Combined, the results highlight the complexity of U biogeochemistry in dynamic, evolving,
514 environmental systems. This complexity, and how it can be modelled at the macro-scale, needs to be
515 considered for contaminated sites and in nuclear waste disposal.

516

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526

527 SUPPORTING INFORMATION

528 Contains additional information on sediment, groundwater, metaschoepite, and microbial community
529 characterization / composition, methods / techniques, pH data, and XAS data.

530

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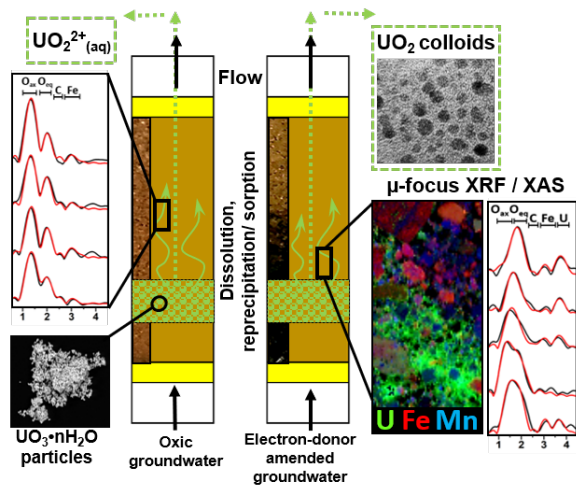
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